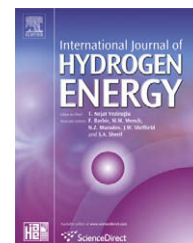


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# The influences of some additives on electrochemical behaviour of nickel electrodes

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## ABSTRACT

Nickel hydroxide is used as an active material in positive electrodes of rechargeable alkaline batteries. Since the nickel hydroxide electrode exhibits a poor performance which results not only from the competitive reactions of the oxidation of the active material but also from the evolution of oxygen. Its reduced charge acceptance is suspected to be related to a relatively long distance between nickel hydroxide particles and the nearest portion of the substrate. The practical capacity of the positive nickel electrode depends on the efficiency of the conductive network connecting the  $\text{Ni}(\text{OH})_2$  particle with the current collector.

In this study, a pasted-type electrode is prepared using spherical nickel hydroxide powder as the main active material on a foamed nickel grid as a current collector. The effects of additives such as metallic cobalt powder, cobalt hydroxide, calcium carbonate and cobalt powder with calcium carbonate on the electrode performance are examined. The calcium carbonate addition increases the oxygen evolution potential while the metallic cobalt powder and its compounds enhance the conductivity of the active material.

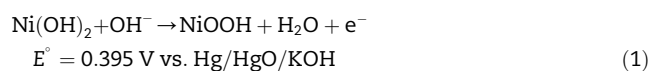
This combined effect in nickel hydroxide electrode in turn increases the capacity of the Ni–MH battery due to the augmentation in the utilization of the active material of the positive electrode.

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## 1. Introduction

With the increasing demand for portable electronic devices and electric vehicle applications, much interest is focused on the development of alkaline batteries with higher specific energies [1–3] in which battery chemistry plays a crucial role. In particular, the development and commercialization of nickel/metal hydride (Ni–MH) technology provide the possibility of producing batteries with high specific energy. This is because the metal hydride, negative electrode, has a higher capacity per unit volume and longer cycle life than the cadmium negative electrode in Ni–Cd batteries [4–6]. The

positive nickel electrode strongly influences the performance of the alkaline batteries. In these batteries, the capacity of the negative electrode is greater than that of the positive electrode and hence the cell capacity is limited by the positive electrode. For Ni–MH cells, the performance of the nickel electrode is to be sufficiently improved to match the superior properties of the negative, namely the hydrogen storage alloy electrode. The active material in the nickel electrode has a theoretical specific capacity of  $289 \text{ mAh g}^{-1}$  according to the equation



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But in practice, the specific capacity of this electrode in the battery is below this value [7]. The preparation of a high performance nickel electrode becomes important and urgent. These objectives could be achieved by selecting the proper conditions for the synthesis of high performance active material by employing proper additives that could provide the conductive network to enhance the utilization of the nickel hydroxide. The reversibility of the Ni(II)/Ni(III) electrochemical reaction could be increased by the incorporation of additives. Further it could inhibit aging effects involving unstable Ni hydroxide species and increase the polarization of the oxygen evolution reaction [8–11].

Many studies have revealed that incorporation of compounds containing transition metal atom, such as cobalt compounds, into the nickel electrode is an effective approach to improve active material utilization and cycle life [12–20]. The cobalt compound reduces both the oxidizing and reducing potentials of the nickel electrode and increases the over potential of oxygen evolution, thus the utilization of the active material is improved [18,19]. A pasted nickel electrode had been developed by adding CoO to yield high active material utilization to a level higher than that presently available with a sintered nickel electrode [16] and the effects of the addition of other calcium compounds like  $\text{Ca}(\text{OH})_2$ , CaS and  $\text{CaF}_2$ , on the nickel electrode of a Ni–MH battery for electric vehicles have also been investigated [19]. It was found that calcium could raise the oxygen evolution potential and hence increase the charge acceptance of the nickel electrode and also inhibit the swelling of the nickel electrode during cycling [21,22].

In the present study the influence of metallic Co powder,  $\text{Co}(\text{OH})_2$ ,  $\text{CaCO}_3$  and simultaneous addition of Co powder and  $\text{CaCO}_3$  on the electrochemical performance and structure of the nickel electrodes is investigated and the results are reported.

## 2. Experimental

### 2.1. Preparation of nickel hydroxide

The chemical synthesis of nickel hydroxide was achieved in three steps viz. (i) addition of the reagents, (ii) digestion of the precipitate and (iii) drying and grinding of the precipitate. There are various methods for the synthesis of nickel hydroxide powder. The method which has been followed in this study is described below. Analar grade KOH and  $\text{NiSO}_4$  were used as reagents. Triple distilled water was used for the solution preparation and washing of the precipitate. A solution of 1 M KOH was added to 1 M  $\text{NiSO}_4$  solution by dripping at a flow rate of  $10 \text{ ml min}^{-1}$  with constant stirring. The addition of the reagent was terminated when the pH of the suspension reaches 13. Then the mixture was allowed to stand for 24 h for digestion of the precipitate. The separation of the precipitate from the excess reagent was done by centrifugation at 1500 rpm for 1 h. The precipitate was washed thoroughly with triple distilled water.  $\text{BaCl}_2$  (1 M) in excess was added to wash water, causing precipitation of  $\text{BaSO}_4$ . The washing of the precipitate was concluded when the white precipitate of  $\text{BaSO}_4$  was no more found in the wash water. This nickel hydroxide precipitate was dried at  $60^\circ\text{C}$  for 72 h.

Finally the precipitate was pulverized and sieved. The material with a particle size of the  $50 \mu\text{m}$  was chosen for electrode preparation.

### 2.2. Preparation of nickel hydroxide electrodes

Because of the poor electric conductivity nickel hydroxide powder alone cannot be used for electrode fabrication. Certain amount of conductive material, e.g. acetylene black, is added to the electrode material. Because of its chain structure, low density and good water absorption characteristics, acetylene black can increase the void and electrode surface per unit volume, and thus improve the contact of the active material with the electrolyte solution. Therefore, increasing the content of acetylene black will improve the utilization. On the other hand, when the  $\text{Ni}(\text{OH})_2$  content is too high the electrode resistance becomes excessive, the utilization of the active material goes down that will in turn decrease the capacity of the electrode material. So a mere increase in  $\text{Ni}(\text{OH})_2$  content will not improve the utilization efficiency. Furthermore, conductive material decreases with increase in the  $\text{Ni}(\text{OH})_2$  content, which hinders the electron transfer between  $\text{Ni}(\text{OH})_2$  particles, i.e. the internal resistance becomes more and thus the capacity decreases [23]. It is impossible to prepare the electrodes without polytetrafluoroethylene (PTFE) solution, because a certain amount of binder is necessary to bind the particles effectively. Increasing PTFE solution content enhances the utilization. Although it increases the specific electrode capacity, further increase in PTFE beyond certain limit will decrease the capacity because of the increase in internal resistance. An optimum amount of PTFE solution produces a fibrous structure that holds the active material powder [24]. After considering all the above factors, the following composition of the electrode material was arrived at: 80%  $\text{Ni}(\text{OH})_2$  powder, 12% nickel powder, 7% acetylene black and 2–5% PTFE solution. Similar compositions have been suggested by others [25–27].

The test electrode was made by first mixing the prepared sample nickel hydroxide powder with acetylene black and PTFE solution in the form of slurry. The resulting slurry was packed into a sponge like nickel porous body support (INCO Nickel FOAM) which has a porosity of 95%. The resulting electrode was dried at  $65^\circ\text{C}$  and pressed under 25 mPa to a thickness of 1 mm. The electrodes have the following dimensions:  $2 \text{ cm} \times 2 \text{ cm} \times 0.1 \text{ cm}$ . Studies were carried out using the following types of electrodes: (i) nickel hydroxide with no additives, (ii) nickel hydroxide with 5% cobalt hydroxide incorporated directly into the slurry, (iii) nickel hydroxide with 5% cobalt powder incorporated directly into the slurry, (iv) nickel hydroxide with 5% calcium carbonate incorporated directly into the slurry and (v) nickel hydroxide with 5% cobalt metal powder and 5% calcium carbonate incorporated directly into the slurry.

### 2.3. Test procedure

For all the experimental measurements, a three compartment glass cell was used. A hydrogen storage alloy electrode with a capacity well in excess of the nickel electrode was used as a counter electrode. A single nickel test electrode was

sandwiched between two metal hydride electrodes with a thin film of cel-gard separator (Hoechst Celanese Corporation, USA) and the assembly was immersed in 30% aqueous KOH solution. Hg/HgO/KOH electrode was employed as a reference electrode. Constant current charge/discharge experiments were performed by using an automatic life cycle tester LCN Bitrode Model 2-10-12. The test cell was charged for 14 h at C/10 rate and kept for 30 min at open circuit condition and then discharged at the C/10 rate to 1.000 V vs. a metal hydride electrode. The same procedure was adopted for three cycles until the discharge capacity became constant. Charge/discharge experiments were conducted only after the test cell reached a stable condition. Usually the cells attain the stable capacity within three cycles. This is called as formation of electrodes. The purpose of the electrode formation is to give the active material an electrochemical exercise by an oxidation–reduction process which has the effect of increasing the lattice defects and surface area of the active material and removal of impurities and loose particles. This electrode formation is essential to maximize the electrode performance.

Voltammetric and AC impedance measurements were carried out using BAS-Zahner IM6 impedance analyzer. Electrochemical impedance spectroscopy (EIS) is an effective technique for analyzing the internal structures and structural change during cycling [28–30]. AC impedance studies of nickel electrode with and without addition agents were carried out. Cyclic voltammetry (CV) is a useful electrochemical technique for investigating electrode/electrolyte interface and superficial charge distribution under potentiodynamic conditions further from equilibrium. Cyclic voltammograms obtained for different types of nickel electrodes have already been reported [25]. For CV studies, the test electrode prepared as described above was used as a working electrode. The counter electrode was a platinum foil and a Hg/HgO/KOH electrode was used as a reference. Prior to CV studies the electrodes were activated in 30% analar grade aqueous KOH solution. After resting for 30 min the cyclic voltammograms were obtained. The scan potential varied from 100 mV to 700 mV vs. Hg/HgO/KOH.

The crystal structure of the active material nickel hydroxide was determined by X-ray diffraction (XRD) using X-ray diffractometer (PANalytical Make, X'per PRO Model, Cu K-2.2 kW Max., Source). Electron microscopic observations were carried out using a scanning electron microscope (HITACHI Model S-3000H). Fourier Transform Spectroscopy (FTIR) absorption spectra for  $\beta$ -nickel hydroxide were obtained using Nexus 670 (FTIR), Centaurms 10 $\times$  (microscope) Model by Thermo Electron Corporation, USA.

### 3. Results and discussion

#### 3.1. Effects of additive on active material structure

Fig. 1 shows a typical example of XRD for nickel hydroxide synthesized by this method. In comparison with JCPDS cards [31,32] it was verified that  $\beta$ -nickel hydroxide was formed in this synthesis. The interlayer distance ( $d$ ) and the relative intensities were in full agreement with those corresponding to  $\beta$ -nickel hydroxide [31]. The peak enlargement can be attributed to the small crystallite size. Then the X-ray measure

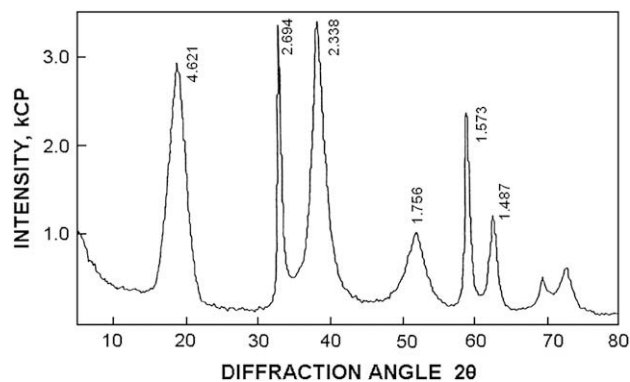


Fig. 1 – XRD pattern for nickel hydroxide.

showed that very small crystallites were formed in the  $\beta$ -nickel hydroxide powders.

Fig. 2 shows the XRD pattern for nickel electrodes with cobalt powder and calcium carbonate additives. There are a few differences between the two patterns. The breaking and broadening of some peaks in Fig. 2 show that the crystal structure of the electrode containing additive is more disordered than that with no additive. The activity of nickel hydride is associated with its crystal structure [32]. In the XRD patterns, the width of the several peaks indicates that their degree of crystallinity is different. It is found that the broader the XRD peak, the greater is the charge capacity. In the figures it is seen that the crystal structure of the electrodes containing additives is more disordered than that with no addition. The electrochemical activity of the nickel hydroxide depends on its crystal structure [33,34].

Fig. 3 shows scanning electron micrographs of spherical nickel hydroxide and electrodes with Co and Co + CaCO<sub>3</sub> additives. It is seen from the figures that the particles of active material with no additive are relatively larger and are agglomerated. By contrast the particles of the active material containing the additive are nearly spherical and quite small. So there is a good inter-particle contact between the particles for better electric conductivity and greater charge acceptance. Because of the higher charge acceptance, discharge potential and depth of discharge, the utilization of active material in

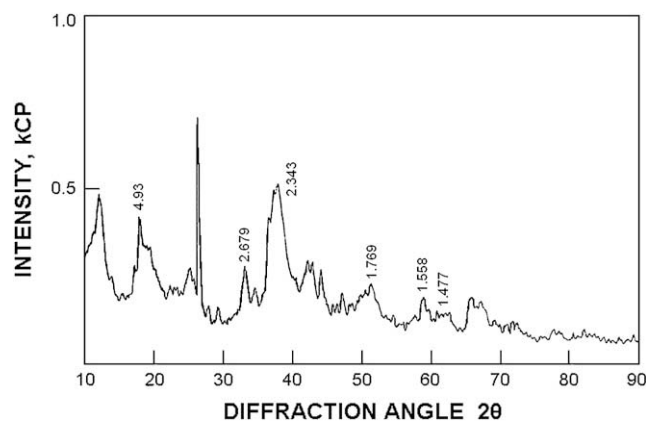


Fig. 2 – XRD pattern for nickel electrodes with cobalt powder and calcium carbonate additives.

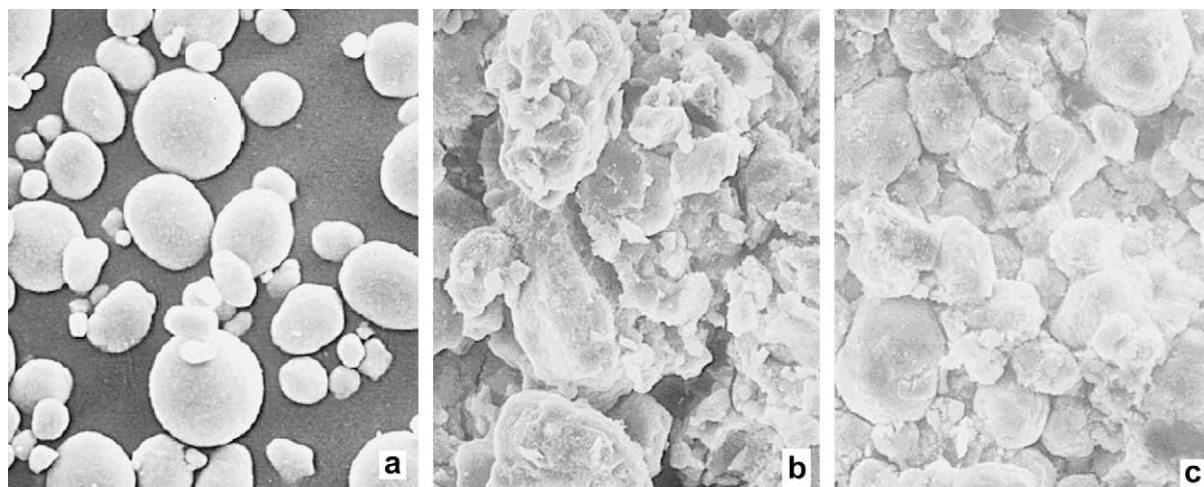


Fig. 3 – Scanning electron micrographs of (a) spherical nickel hydroxide and (b) with Co (c) with Co+ CaCO<sub>3</sub>.

nickel electrode containing cobalt + calcium carbonate is higher than that with no additive.

FTIR absorption spectra for  $\beta$ -nickel hydroxide are shown in Fig. 4. It shows the characteristic bands for sulphate, carbonate and adsorbed water. Table 1 shows the absorptions bands and their attributions [35,36]. The presence of carbonate is due to the open system used in active material synthesis.

### 3.2. Effects of additive on the electrochemical performance

The specific capacities of the electrodes with no additive, with cobalt, cobalt hydroxide, calcium carbonate and with simultaneous addition of metallic cobalt powder and calcium carbonate all prepared under same condition are listed in Table 2.

The specific capacities of the active material with simultaneous addition of Co and calcium are higher than that of the active material with only Co and also with only addition of calcium, particularly at higher discharge rates. From Table 1 it is found that the capacities of the nickel electrode containing calcium increase gradually with discharge rate and the decrease is very slow at higher rate.

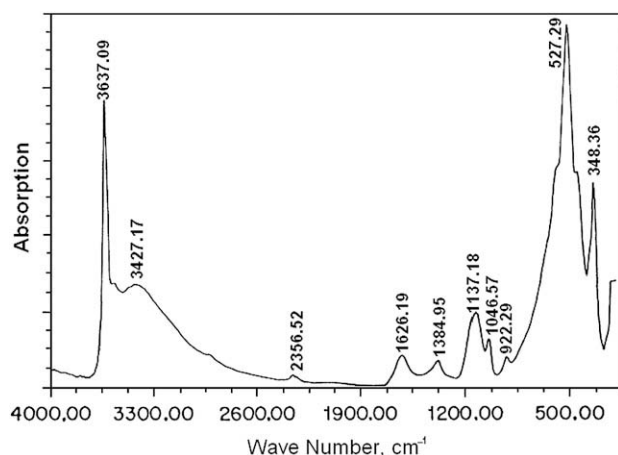


Fig. 4 – FTIR absorption spectra for beta nickel hydroxide.

The charge/discharge characteristics of nickel electrodes, without addition and with Co, Co(OH)<sub>2</sub>, CaCO<sub>3</sub> and Co + CaCO<sub>3</sub> at C/5 rate are shown in Fig. 5. The redox reaction of the nickel electrode is expressed as given in Eq. (1). But here it should be noted that the oxygen evolution occurs at an electrode potential above +0.400 V vs. Hg/HgO which is slightly above the open circuit potential of nickel hydroxide electrodes. Thus the oxygen evolution cannot be avoided during charging process according to the following reaction:



For an electrode with no additive, the oxygen evolution reaction takes place easily and this will lower the charging efficiency. With addition of Co and calcium compounds, however, the oxygen evolution potential increased markedly (Fig. 5a). This effect hinders the oxygen evolution reaction and increases greatly the charging efficiency and thus more utilization of active materials. The effects of cobalt, Co(OH)<sub>2</sub>, CaCO<sub>3</sub> and Ca(OH)<sub>2</sub> + CaCO<sub>3</sub> are investigated. The effect of

Table 1 – FTIR–The attributions of the absorptions bands.

Wave number (cm <sup>-1</sup> )	Attributions of the absorption bands
3637	Vibrational stretching of hydroxyl group in the nickel hydroxide lattice
3427	Vibrational stretching of hydroxyl group of the adsorbed water
2356	CO <sub>2</sub> present in the air
1626	Water angular deformation
1384 and 1046	Carbonate anion vibration stretching
1137 and 922	Sulphate anion
527	Water angular deformation in plane
457	Ni–O vibrational stretching
348	Water angular deformation outside of plane

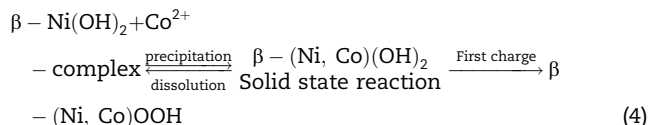
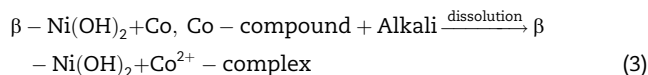


**Table 2 – Specific Discharge Capacity of various active materials.**

Discharge rate	Specific capacity (mAh g <sup>-1</sup> )				
	With no additives	With additives			
		Co	Co(OH) <sub>2</sub>	CaCO <sub>3</sub>	Co and CaCO <sub>3</sub>
C/10	210	230	200	225	236
C/5	190	200	190	230	238
1 C	150	180	170	215	222

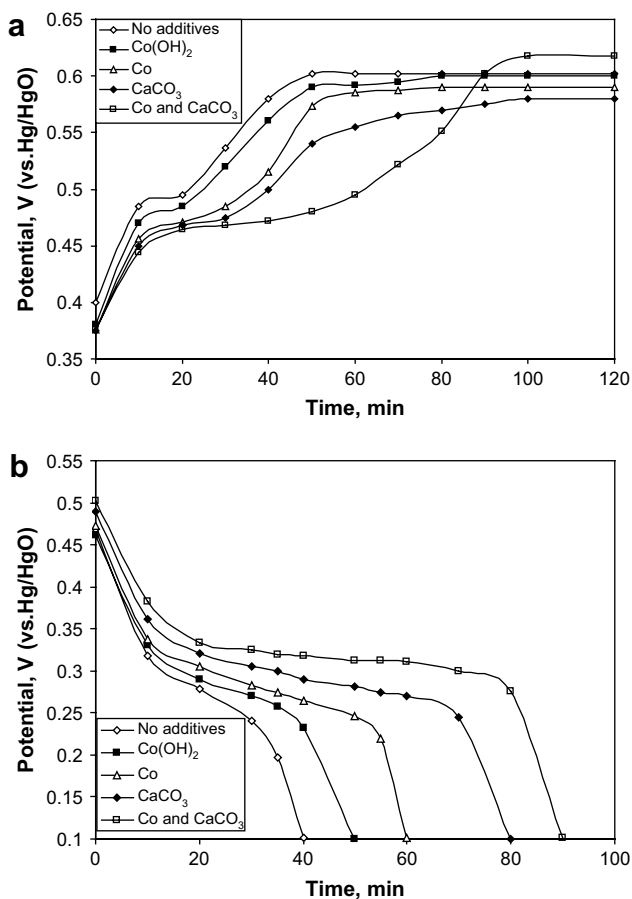
cobalt addition can be attributed to the solid state reaction by decreasing the charge transfer resistance of nickel electrode reaction [37,38]. The practical capacity of the positive nickel hydroxide electrode depends on the efficiency of the conductive network connecting the nickel hydroxide particles with the current collector. The conductive network may be divided into a coarse part and a fine part. In the case of so-called pressed mass electrodes the coarse part usually consists of nickel hydroxide powder. The fine part is established by cobalt oxy-hydroxide, CoOOH, which is an electrical conducting Co<sup>3+</sup> compound that is electrochemically formed from Co<sup>2+</sup> compound (CoO, Co(OH)<sub>2</sub>) during the first charge in an alkaline medium. Like the addition of nickel powder, this was considered to be due to the distribution of isolated cobalt

oxy-hydroxide particles that did not sufficiently connect nickel hydroxide with the adjacent substrate. It was therefore considered that the formation of cobalt oxy-hydroxide in situ in the cell through a dissolution–precipitation process could be effective, since this was expected to provide continuity of a good electrical path.

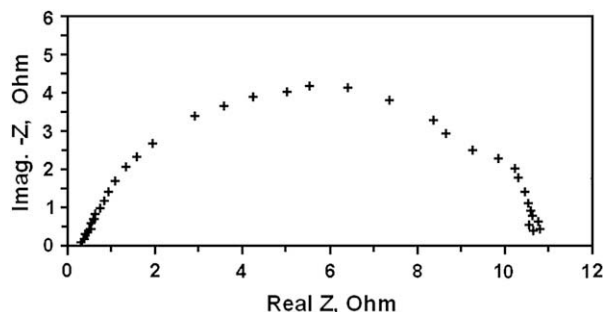


β-CoOOH is well spread at the surface of the nickel hydroxide particles and ensures a very efficient conductive network leading to a higher utilization of the nickel hydroxide by improving the proton conductivity of nickel hydroxide [33,36–39], decreasing the electric resistance and hence increasing the high rate discharge performance. β-CoOOH is considered to be a stable compound that cannot be reduced during usual discharge cycles. However, if the electrochemical potential at the nickel hydroxide electrodes decreases far below its usual working potential of about +350 mV vs. Hg/HgO, the conductive network β-CoOOH may be electrochemically reduced to poor soluble Co(OH), or even to Co, resulting in a deteriorated fine part of the network. The reduction of β-CoOOH commences thermodynamically below a potential of +90 mV vs. Hg/HgO/KOH.

From Fig. 5a and Table 2 it can be seen that the metallic cobalt additions are superior to Co(OH)<sub>2</sub> additions. This is related to the good conductivity of Co. A characteristic weakness of the nickel electrode is the reduced charge acceptance at elevated temperature, which is consequently eliminated, at least partly, by cobalt addition. The structure of nickel hydroxide is dependent not only on the history of the electrode material but also on additives like cobalt and calcium compounds. Cobalt promotes a more complete oxidation of Ni(OH)<sub>2</sub>. Furthermore, cobalt stabilizes the nickel hydroxide and reduces self-discharge at elevated temperature. Calcium compound addition increases the oxygen over potential. Fig. 5b shows the discharge characteristics of nickel electrodes with and without additives. From the figure it is observed that the addition of Co + CaCO<sub>3</sub> enhances the discharge output of the electrodes. The impedance spectra of



**Fig. 5 – (a) The charge characteristics of nickel electrodes with and without additives at C/5 rate. (b) The discharge characteristics of nickel electrodes with and without additives at C/5 rate.**



**Fig. 6 – The impedance plot of nickel hydroxide electrodes with no additive.**

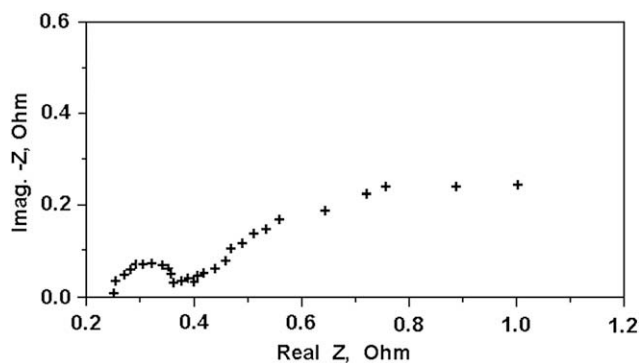


Fig. 7 – The impedance plot of nickel hydroxide electrodes with the addition of Co and CaCO<sub>3</sub>.

nickel hydroxide electrodes with no addition and those with Co and CaCO<sub>3</sub> are shown in Figs. 6 and 7. From the spectra it is observed that the impedance of the electrode with no additive is larger and this prevents the complete discharge. But with the additives, the impedance of the electrode is small and thus permits higher discharge rates.

Fig. 8 presents the voltammograms for electrodes with and without additives. From the voltammogram it is seen that the addition increases both the oxidation and the reduction peak currents. This shows that the addition of cobalt as well as Co + CaCO<sub>3</sub> causes a marked improvement in capacity and reversibility between the oxidation and reduction states. Furthermore, the reduction potential of the electrodes with additives is lower for the same current density i.e. the addition suppresses the polarization. Thus the electrodes with Co + CaCO<sub>3</sub> are more suitable where high rate discharge capabilities are expected.

Typical constant current discharge curves of the cells with addition and without addition at various temperatures (30 °C, 0 °C, –20 °C) at C/5 rate are shown in Fig. 9(a–c). The discharge curves show that the incorporation of cobalt and cobalt with calcium carbonate into the electrode invokes excellent discharge behaviour. Discharge curves for electrode with additives exhibit the longer plateau and the highest coverage discharge capacity output. Even at lower temperatures, 0 °C

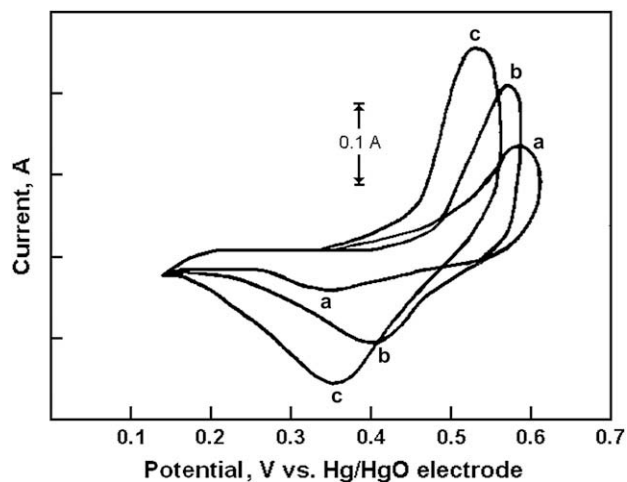


Fig. 8 – Voltammograms for electrodes at scan rate of 1mv s<sup>-1</sup> with (a) no additive (b) Co and (c) Co + CaCO<sub>3</sub>.

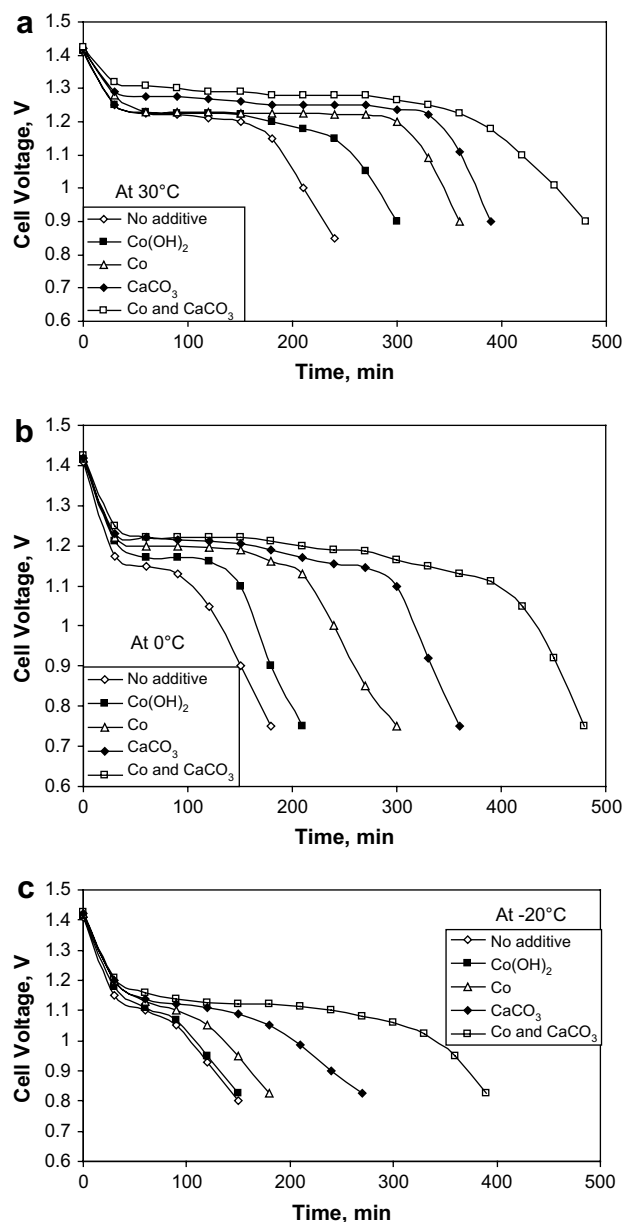


Fig. 9 – Constant current discharge curves of the cells with addition and without additives at various temperatures at C/5 rate are (a) 30 °C, (b) 0 °C and (c) –20 °C.

and –20 °C, the electrode with cobalt + calcium carbonate has the best beneficial effect on the discharge curves.

Fig. 10 shows the cycle life performance of the various types of electrodes under study. The figure clearly shows that electrodes with Co and Co + CaCO<sub>3</sub> additives not only have higher discharge capacity but also exhibit superior stability of capacity during prolonged charge/discharge cycling. Due to the addition of Co and Co + CaCO<sub>3</sub> the oxygen evolution is inhibited during charging. Thus the charge efficiency and the discharge efficiency are increased. The simultaneous addition of cobalt and calcium carbonate improves the utilization and discharge potential of the positive active material. Calcium has been found to raise the oxygen evolution over potential. Cobalt addition has been found to improve both the electronic and the protonic conductivity of

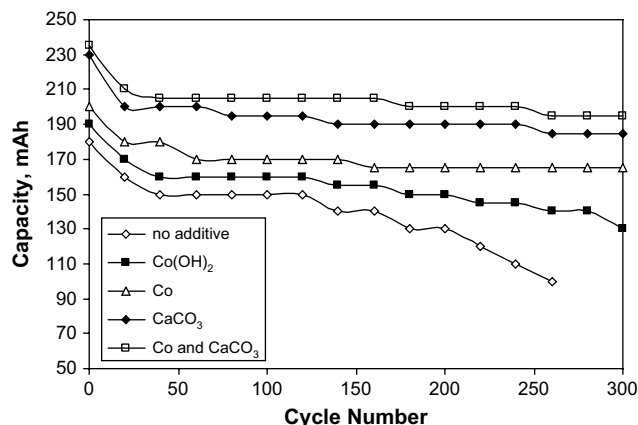


Fig. 10 – The cycle life performance of the various types of electrodes under study at C/5 rate.

the electrode. Both the effects increase the charge acceptance and the discharge depth of the nickel electrodes.

Moreover it is well known that the swelling of the nickel electrodes during cycling has detrimental effect on the performance of nickel electrodes and batteries. Swelling is related to the formation of  $\gamma$ -NiOOH during cycling. This is especially true when the electrodes are subjected to over-charging. The addition of Co and Ca compounds suppressed the formation of  $\gamma$ -NiOOH and swelling of the electrodes by lowering the charging potential and thus increasing the charge acceptance. This is very well seen in the charge/discharge curves (Fig. 5a and b).

#### 4. Conclusions

In this study, a pasted-type electrode is prepared using spherical nickel hydroxide powder as the main active material on a foamed nickel grid as a current collector. The effects of additives such as metallic cobalt powder, cobalt hydroxide, calcium carbonate and cobalt powder with calcium carbonate on the electrode performance are examined. Analysis of the experimental results shows that the incorporation of metallic cobalt powder into the electrode invokes excellent charge/discharge behaviour. Furthermore, discharge curves for electrodes with cobalt exhibit the largest plateau and the highest average discharge voltage. Electrochemical testing and structure analysis of nickel electrodes with and without the addition of calcium carbonate show that oxygen evolution during charging process is inhibited by the use of calcium addition. Thus the charge efficiency is increased. The simultaneous addition of metallic cobalt and calcium carbonate can improve markedly the utilization and discharge potential of the positive active material. Calcium has been found to raise the oxygen evolution potential. On the other hand, cobalt addition has been found to improve the electronic conductivity of the electrode. This combined effect in nickel hydroxide electrode in turn increases the capacity of the Ni-MH battery due to the augmentation in the utilization of the active material of the positive electrode result in superior charge acceptance, long cycle life and higher depth of discharge of the nickel electrode.

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